

munication with the channels to provide increased accessible catalyst surface and, preferably, an absence of small pores for high temperature stability and strength. Whereas the superficial surface area of such structures may be of the order of 0.001 to 0.01 m.²/g. including the channels, the total surface area is typically many times greater, so that much of the catalytic reaction will take place in the large pores. The skeletal structure can have a macropore distribution such that at least 95% of the pore volume is in pores of a size, i.e., a diameter, of over 2,000 Å. and at least 5% of the pore volume is in pores having a size of over 20,000 Å. In a preferred embodiment at least 20% of the pore volume is in pores of a size over 20,000 Å. The support can have other pore distributions as long as the total pore volume indicates a structure having at least 0.03 cc./gm., preferably at least 0.1 cc./gm., in pore volume. Thus, at least 95% of the pore volume can be in macropores of over 200 Å. in size. Also some portion of the pore volume, for instance, at least about 5%, can be in pores of at least 2,000 Å. in size. Generally, the total surface area, that is including the pores, of the support or carrier of the present invention as distinguished from the apparent surface area, is at least about 0.08 square meter per gram, preferably about 0.2 to 2 square meters per gram. The geometric superficial or apparent surface area of the carrier including the walls of the openings should be as large as is consistent with an acceptable back pressure in the fluid flow system. Ordinarily, in the treatment of auto exhaust gases, the volume of catalyst and the superficial surface area are adjusted to a back pressure of less than about 10 pounds per square inch, and preferably less than about 5 pounds per square inch, at maximum acceleration. The superficial area will often be about 0.5 to 6, preferably 1 to 2.5, square meters per liter of support.

Thus, the openings through the body can be of any shape and size consistent with the desired superficial surface and should be large enough to permit free passage of the fluids to be reacted and to prevent plugging by particulate matter that may be present in the fluids as, for instance, lead compounds. In one embodiment, the channels or openings are generally parallel and extend through the support from one to an opposite side, such openings being usually separated from one another by preferably thin walls defining the openings. In another embodiment, a network of channels permeates the body. The channels are unobstructed or substantially unobstructed to fluid flow. For most efficient operation, the openings are distributed across essentially the entire face or cross-section of the support subject to initial contact with the fluid to be reacted. The preferred supports or carriers are zircon-mullite characterized by having good thermal shock resistance because of its low coefficient of thermal expansion, and alpha-alumina although other similar chemically-inert refractory crystalline ceramic materials can also be employed. Examples of other refractory materials suitable as a support or carrier are, for instance, sillimanite, magnesium silicates, zircon, petalite, spodumene, cordierite, aluminosilicates, mullite, etc. Any of these usually essentially crystalline materials may be formed into refractory bodies as may be desired in a mix with a minor amount of a binder. Suitable binders include clays for instance ball clays, calcium carbonate, magnesium aluminum silicates (V-gums) and Na₂SiO₃ either used alone or in a balanced combination.

The catalytically-active metal oxide is deposited on the external surface of the unitary skeletal support as a continuous thin deposit or as discontinuous thin deposit usually at a thickness of about 0.0001 to 0.005 inch, preferably 0.0004 to 0.001 inch, and when mixed with platinum group metal, makes up the film or coating on the support of the invention. The catalytically-active refractory metal oxide is characterized by a porous structure which possesses a large internal pore volume and

total surface area. Its presence in the catalyst of the invention is important since impregnation of the carrier directly with the platinum group metal provides an unsatisfactory catalyst. Generally, the total surface area of the active refractory metal oxide film will be at least about 25 square meters/gram, preferably at least about 100 square meters/gram. Such oxides can be prepared by at least partially, preferably substantially completely, dehydrating and thus activating the hydrate form of the oxide by calcination usually at temperatures of about 150° to 700° C. or 800° C. or somewhat more. The preferred active metal oxide films contain members of the gamma or activated alumina family which can be prepared, for instance, by precipitating a hydrous alumina gel and thereafter drying and calcining to expel hydrated water and provide the active gamma-alumina. A particularly preferred active refractory metal oxide is obtained by drying and calcining at temperatures of about 300° to 700° or 800° C. a mixture of precursor hydrous alumina phases predominating in crystalline trihydrate, that is, containing in excess of about 50% of the total alumina hydrate composition, preferably about 65 to 95% of one or more of the trihydrate forms gibbsite, bayerite and nordstrandite (previously known as randomite) by X-ray diffraction. The substantial balance of the hydrate, i.e., at least 5% preferably about 5 to 35%, may be amorphous hydrous or monohydrate (boehmite) alumina. Calcination of the precursor hydrous alumina is preferably controlled so that the gamma-alumina obtained contains monohydrate alumina in an amount substantially equivalent to that originally present in the mixture of the high trihydrate precursor hydrous alumina phases. Other suitable active metal oxides include for example, active or calcined beryllia, zirconia, magnesia, silica, etc., and combinations of metal oxides such as boria-alumina, silica-alumina, etc. Preferably the film is composed predominantly of oxides of one or more metals of Groups II, III and IV having atomic numbers not exceeding 40. The concentration of the active refractory metal oxide film is usually about 15 to 150 grams per liter of the unitary support, preferably about 30 to 75 grams per liter.

Providing the support with a coating or layer of the calcined or active refractory metal oxide of the present invention can be accomplished in several ways. One method comprises dipping the support into a solution of the salt of the chemically active refractory metal and calcining to decompose the salt of the oxide form. This method generally necessitates several similar dippings, however, before a satisfactory film or layer is obtained. A more preferred method comprises dipping the support into an aqueous suspension, dispersion or slurry of the refractory oxide itself, drying and calcining. In this method, while suspensions or dispersions having a solids content in the range of about 10 or 30 to 70% by weight can be used to deposit a suitable amount of an active refractory metal oxide on the support in a single application, it is preferred that they contain about 15 to 50% by weight of solids. Dispersions containing over 50% by weight of solids in many instances are too viscous for the coating or film producing process. In order to prepare a catalyst having 10% activated alumina on a zircon-mullite structure, for example, about 20-40% solids in suspension may be used. A particularly preferred method involves forming an aqueous dispersion or slurry as just described and subjecting the mixture to a wet grinding or milling operation whereby the refractory metal oxide is reduced to a finely divided form and a thixotropic slip is obtained, having the desired consistency, with a solids content as noted above. The support is then dipped into the slip, dried and calcined. In general, calcining temperatures within the range of about 150 to 700 or 800° C. are employed. The calcination is favorably conducted in air, for example, flowing dried air, or may be carried out in contact with other gases such as oxygen,